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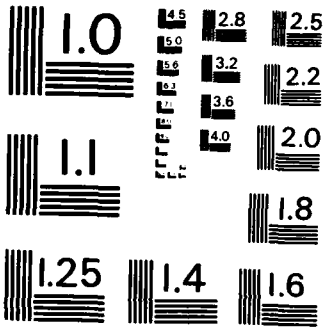

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FABRICATION OF LOW-LOSS HALIDE GLASS FIBERS

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The primary objective of this program was to develop ultralow-loss fibers for use in long-distance Navy communications systems. Accomplishments of that goal were directed toward the investigation of materials that would transmit in the infrared, as well as fiber drawing processes for these materials.

Major emphasis has been placed on fabrication of chloride and fluoride-chloride glasses. These glasses were subsequently doped with a sulfide. Heavy-metal fluoride glasses, which are generally considered to be viable for IR fiber fabrication, are being prepared at Hughes under a contract to NRL. For the present program, two different compositions of CdF_2-$CdCl_2$-BaF_2 were prepared and subsequently doped with either CdS or ZnS. Impure starting materials, devitrification, and steep viscosity curves combined to limit fiber fabrication.

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Continuation of research previously funded by ONR aimed at the growth of single crystal KRS-5 fibers is also discussed. By using single-crystal fibers, both the intrinsic predicted low loss of this material and a reduction in the aging process of fibers extruded from the material were anticipated. A process for producing single-crystal fibers of KRS-5 was indeed developed, but no improvements in the fiber were observed. Although fiber fabrication is necessarily limited by the results of glass formation, materials obtained from other sources were also drawn into fiber in an effort to determine the problems specific to fiber fabrication of IR materials.

An explanation of the KRS-5 aging mechanism based on the most recent experiments is included, along with a comparison of all three research areas.

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SECTION 1

INTRODUCTION AND SUMMARY

The primary objective of this program was to develop ultralow-loss fibers for use in long-distance Navy communications systems. Accomplishments of that goal were directed toward the investigation of materials that would transmit in the infrared and fiber drawing processes for these materials. During the last 12 months this program has addressed the following three tasks:

- Investigation of new infrared transmissive glasses suitable for fiber drawing.
- Evaluation of the optical losses (absorption and scattering) in bulk glasses and fibers.
- Fabrication of Draw fiber from the best IR glasses prepared in Task 1.

Within the first task, major emphasis has been placed on fabrication of chloride and fluoride-chloride glasses. These glasses were subsequently doped with a sulfide. Heavy-metal fluoride glasses, which are generally considered to be viable for IR fiber fabrication, are being prepared at Hughes under a contract to NRL. For the present program, two different compositions of CdF_2-$CdCl_2$-BaF_2 were prepared and subsequently doped with either CdS or ZnS. Impure starting materials, devitrification, and steep viscosity curves combined to limit fiber fabrication. (Specific results are discussed in Section 2.)

The work discussed in Section 3 cover a continuation of research previously funded by ONR aimed at the growth of single crystal KRS-5 fibers. By using single crystal fibers, both the intrinsic predicted low loss of this material and a reduction in the aging process of fibers extruded from the material were anticipated. A process for producing single crystal fibers of

KRS-5 was indeed developed, but no improvements in the fiber were observed. Although fiber fabrication is necessarily limited by the results of glass formation from Task 1, materials obtained from other sources were also drawn into fiber in an effort to determine the problems specific to fiber fabrication of IR materials. This is discussed in Section 3.

An explanation of the KRS-5 aging mechanism, based on the most recent experiments, is included in Section 4, along with a comparison of all three research areas.

SECTION 2

NEW GLASS COMPOSITIONS

A. INTRODUCTION

Previous work on IR transmitting fibers has centered around polycrystalline extruded fibers of KRS-5 and heavy-metal fluoride glass fibers. The KRS-5 fibers have never achieved their expected intrinsically low loss and also suffer from an aging problem. Heavy-metal fluoride glasses also have anamolously high attenuations and aging problems. In addition, the limit of their useful transmission range is approximately only around 8 μm. Attempts to use other systems such as chlorides is restricted because of their hygroscopic character; and chalcogenides are limited because of poor transparency in the near IR, coupled with typically high non-linear refractive indices. Chalcogenide glasses presently used for fiber drawing have low strengths and are brittle.

Although all the previously mentioned systems exhibit some undesireable properties, we attempted to capitalize on our previous experience in handling halides and halide glasses. Personnel at the Hughes Research Laboratories have considerable expertise in reactive atmosphere processing (RAP) treatment of halides. Application of RAP to other halide systems has yielded tremendous improvements in both mechanical and optical properties of laser windows.[1] Consequently,the thrust of this contract was aimed at developing optical fibers that could transmit at 10.6 μm using halide materials. Subsequent purifications by RAP treatment, if necessary could then be carried out to improve optical transmissions.

Based on our previous experience with halide systems, we attempted to optimize the ratio of fluoride and chloride glass compositions to yield transmission to 10.6 μm coupled with good stability and performance in ambient conditions. Successful completion of this task was dependent on high purity starting

materials, proper preparation and handling of the components, and a glass product that could be drawn into a fiber without deterioration in ambient conditions.

B. BACKGROUND

In contrast to the extensive investigations of chalcogenide glass systems, virtually no interest has been shown in the mixed-halide glass systems for IR fiber manufacture. Yet the possibilities for low attenuation systems increase as more highly purified materials become available.

Although many benefits arise from using large mole percentages of halides other than fluorine (F^-), there are distinct tradeoffs which limit their usefulness as IR transparent materials. The primary problem observed with chloride glasses, for example, is their inherent hygroscopic nature. $ZnCl_2$ glass has excellent IR transmission characteristics but will not survive for more than a few minutes in air before crystallizing and becoming completely deliquescent. Although bromide and iodide glasses do not always exhibit this problem, they become limited by their typically low glass transition temperatures (Tg) of <25°C.

In recently published work, Matecki, Poulain and Poulain[2] reported that a relatively stable fluoro-chloride glass based on cadmium and barium has shown a potential transmission out to 11 μm. This mixed-halide system of CdF_2-$CdCl_2$-BaF_2 is attractive not only because of its for IR transparency but also because its large compositional glass-forming region (see Figure 2-1) allows the greatest flexibility in manipulating the individual constituents toward the largest Cl:F ratio possible, while still maintaining the physical properties necessary for fiber fabrication.

In the present study we have examined two glass compositions that differed from each other in the ratio of chloride to fluoride components. Both glasses were doped with

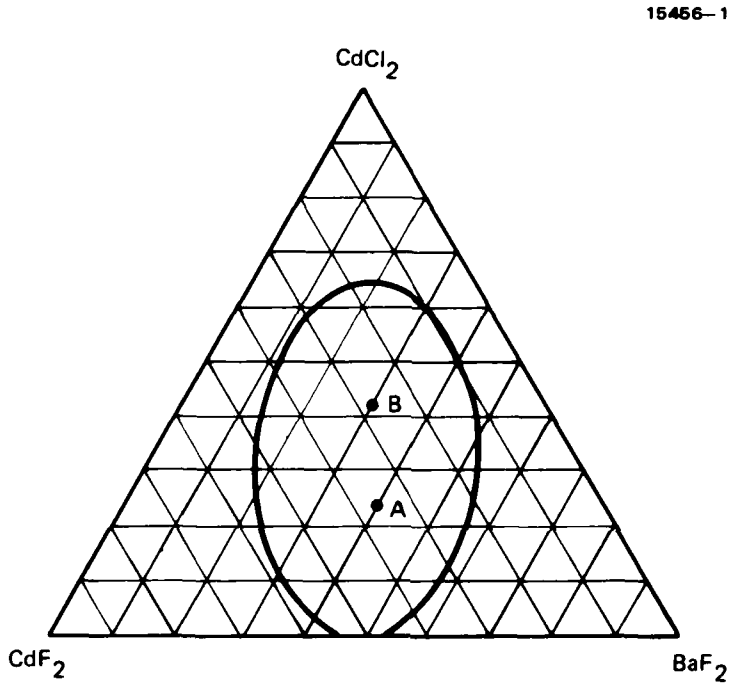

Figure 2-1. Glass forming region in $CdCl_2$-CdF_2-BaF_2 composition diagram.

a small amount of chalcogenide dopant in an attempt to modify the glass networks so that increased amounts of a chloride component could be tolerated. CdS and ZnS were chosen because of their transparency at longer wavelengths and network modifying characteristics.

C. MATERIALS PREPARATION

Initial attempts at preparing infrared transparent glasses for this investigation began with the ternary system outlined in Figure 2-1. The CdF_2-$CdCl_2$-BaF_2 chemical components were originally reagent grade products supplied by a commercial vendor. Glass preparation simply consisted of weighing and mixing the components in the proper proportions, and then transferring them to a silica crucible for melting before subsequent casting into a brass mold.

Two glasses resulted from this procedure with compositions near the center of the glass forming region. Glass [A] was mainly fluoride-based with a molar composition of 34% CdF_2, 26% $CdCl_2$, and 40% BaF_2. An attempt to increase the Cl:F ratio yielded glass [B] which had the composition: 27% CdF_2, 40% $CdCl_2$, and 33% BaF_2. Both of these glasses demonstrated good durability in ambient conditions. Thicknesses of the cast glass ingots were approximately 1.4 mm.

The addition of 6.0% and 3.0% CdS in Glass [A] resulted in a devitrified ceramic upon casting. The highest level tolerated by this glass was 1.5% CdS. Surprisingly, Glass [B] resulted in a devitrified ceramic with any addition of either of the two dopants.

Infrared transmission spectra on two of the glass samples identified the presence of H_2O and OH^- impurities which could be responsible for devitrification of the remaining samples. This information led to the acquisition of a high quality stainless steel dry box. Oxygen and H_2O concentrations in the

inert Argon atmosphere of the dry box were determined to be 1 ppm or less. To further reduce the problem of H_2O contamination, the brass casting mold used for quenching was baked out at 200°C under vacuum in the presence of a Ti-metal getter. This mold was transported under vacuum into the dry box before being reopened. A small resistance-heated pot furnace was introduced into the dry box to melt the prepared samples. All procedures including weighing and mixing were performed inside the dry box.

New samples of Glass [B], and Glass [A]/1.5% CdS were melted and quenched under the inert atmosphere of the dry box. Results were mixed with little or no improvement in the glass forming ability of sulfide-doped samples. Volatility of the prepared samples while melting appeared to increase under the dry conditions. Despite efforts to limit all types of impurity contamination, only a slight improvement was observed.

D. GLASS EVALUATION

Evaluation of the glass samples is based primarily on two independent techniques. In this study, an infrared spectral scan from 2.0 to 20 μm provided information on the impurity absorptions and transparency at the CO_2 laser wavelength of 10.6 μm. Thermal analysis was used to determine the transition temperatures of the glasses--a necessary parameter for evaluating a sample's potential for fiber manufacturing. Thermal analysis was performed by Differential Scanning Calorimetry (DSC) on a DuPont 1090 Thermal Analyzer.

Transmission spectra for Glass [A]/1.5% CdS (Figure 2-2) and Glass [B] (dry box) (Figure 2-3) both had relatively good transmission to approximately 8.0 μm, with OH^- absorption peaks evident at approximately 2.75 μm. A decrease in transmission from 8.0 to 12 μm was followed by an increase in transmission

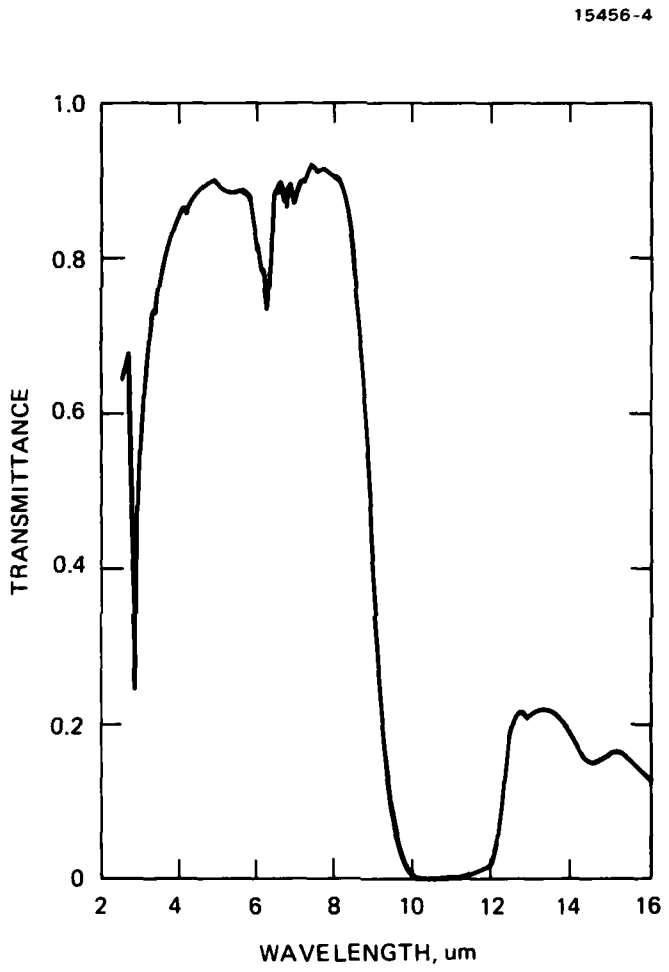

Figure 2-2. Transmission curve for glass [A].

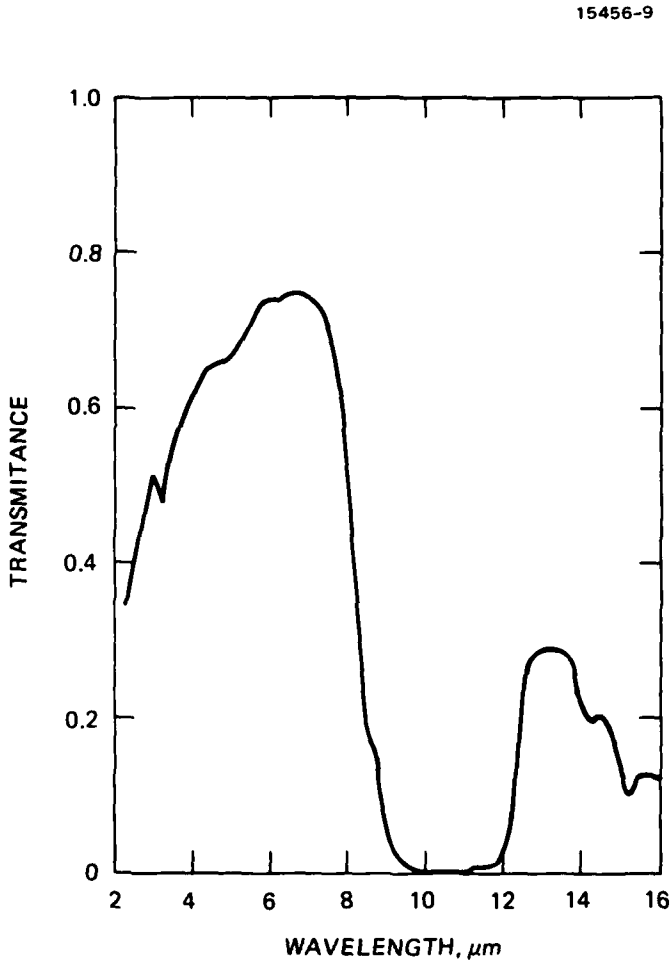

Figure 2-3. Transmission curve for glass [B].

beyond 12.0 μm. This pattern suggests that transmission out to 12.0 μm is possible, but that an absorbing impurity is present in both samples (presumably an oxide).

DSC results of the same two glasses appear in Figure 2-4 together with a thermogram of Glass [B]. These thermograms identify the temperatures at which both exo-and endothermic reactions, such as crystallization, occur in the solid sample. All three samples show multiple crystallization temperatures (T_x) and peaks indicating that isolated impurity phases are present in the network. The broad endothermic peaks just prior to the larger crystallization peaks correspond to the temperature (T_g) where glass softening begins. This is the temperature where fiber drawing takes place. Ideally (T_x-T_g) is large in order to avoid crystallization tendencies during fiber production. Typical values for the prepared samples in this investigation were approximately 25°C. This value is probably too low for successful fiber drawing. Figure 2-5 shows that very little difference is observed between samples which are sulfide doped, undoped, or prepared in the dry box. This lack of difference is attributed to the inability to remove the impurities in any of these samples. Each of the thermograms shows two crystallization peaks. The first corresponds to the halide glass matrix devitrification, followed by the second crystallization peak of the impurity phase. The final peak identifies the melting temperature of the material.

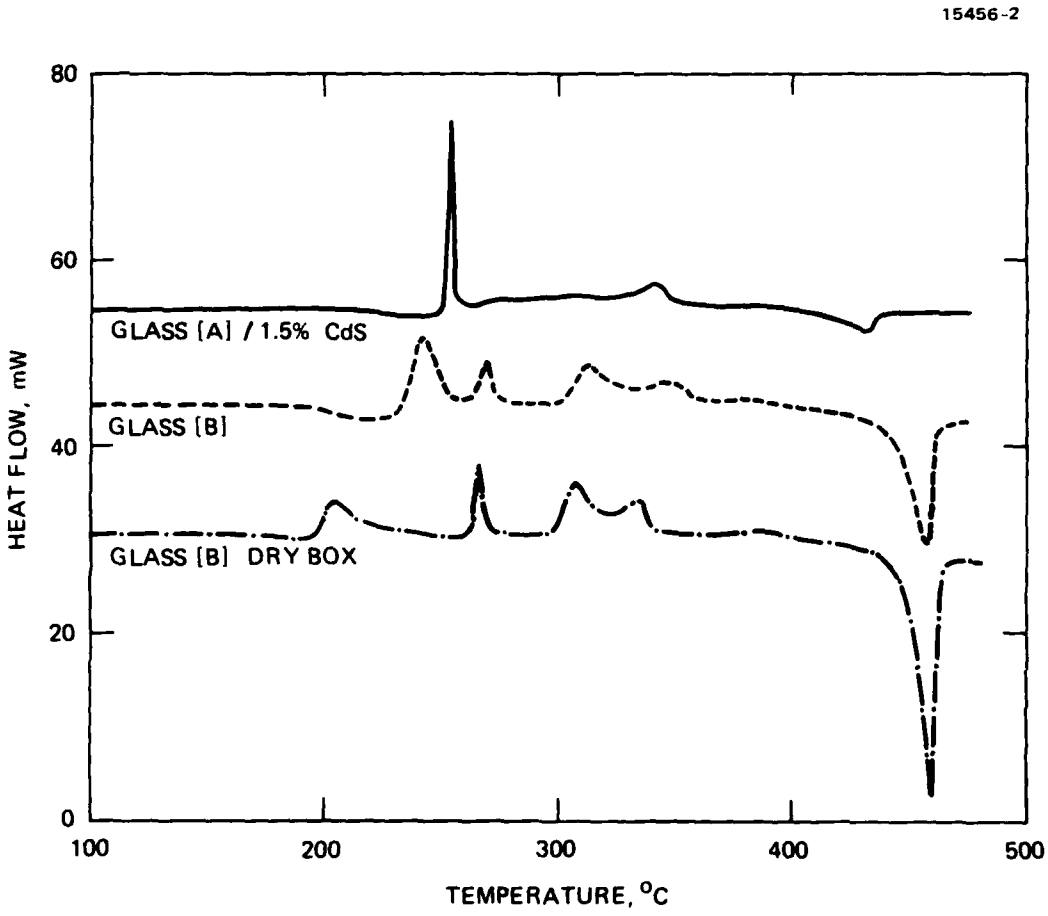

Figure 2-4. Differential scanning calorimetry of glass [A] and [B].

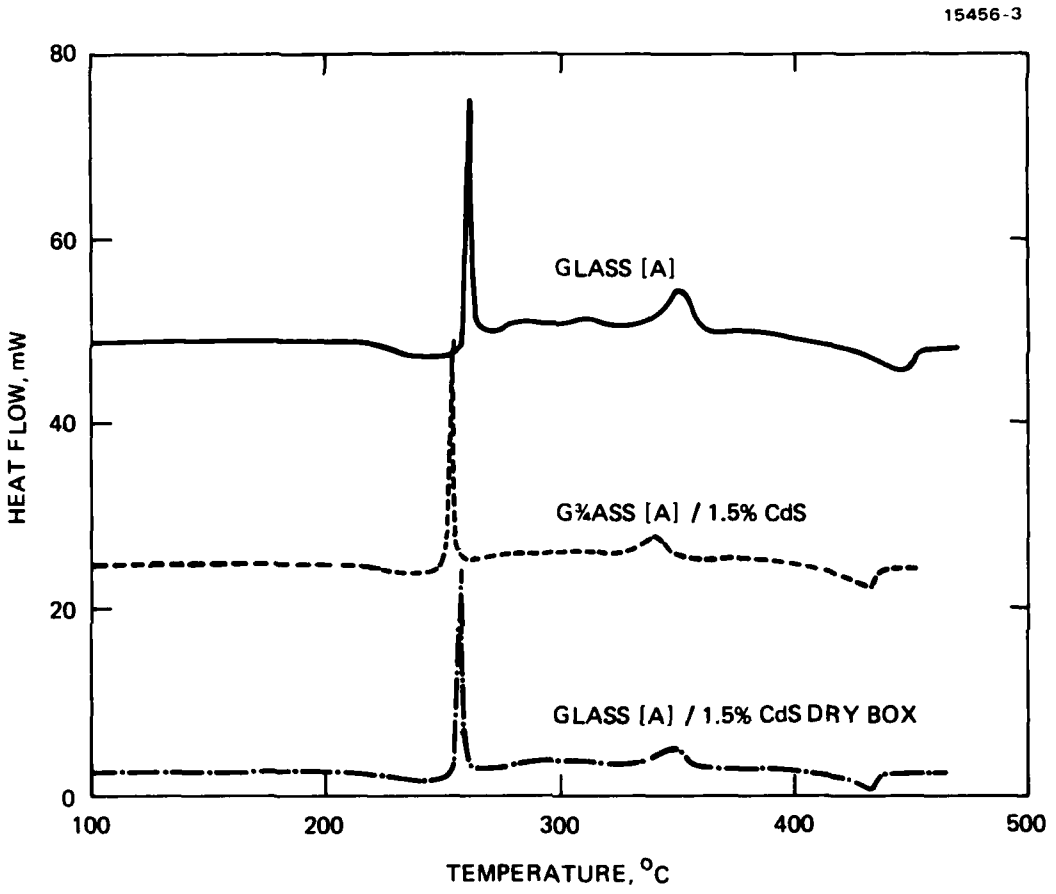

Figure 2-5. Comparison of differential scanning calorimetry curves of glass [A] with doping and dry box preparation.

SECTION 3

FIBER FABRICATION

A. INTRODUCTION

Although the preferred direction of this investigation has been to fabricate suitable chloro-fluoride glasses, other glasses, viz. chalcogenides, have some merit. Well known, also are the polycrystalline halide materials such as KRS-5, TlBr, TlI and AgCl and their single crystal derivatives for infrared transmission.

As mentioned earlier, the chalcogenides considered most suitable for fiber manufacture are difficult to draw into fiber, difficult to handle, and possess nonlinear optical properties, all of which contribute to their undesirability. However, they are known to be transparent in the far infrared and not nearly as sensitive to moisture as the halides.

Since a variety of short length sensor and power delivery applications have already employed some extruded polycrystalline (PC) fibers for infrared transmission, these materials must also be considered. The best PC fiber has a loss of about 200 dB/km, which is far above its theoretical limit, but may be attributed to properties relating to grain boundaries, stress induced during extrusion, and poor surface quality of the fiber.

Fiber fabrication during this contract has incorporated both of these materials by drawing chalcogenide glass bulk material obtained from AMTIR, Inc., and also by passing polycrystalline halide fibers through a traveling melt zone in order to convert them to single-crystal (SC) fibers.

B. SINGLE CRYSTAL INFRARED FIBERS

Previous single crystal fiber growth techniques have, in general, relied on a capillary shaper or edge-definer to configure the fiber diameter. While all the previous

techniques have used a molten reservoir as a source, our traveling zone method melts short lengths of PC fiber locally, resulting in a fiber that is SC.

Instead of beginning with a melt, we begin with a PC fiber that has been fabricated in our extrusion process and sucessfully converted to SC fiber using a traveling zone technique. The advantage of starting with an extruded fiber to produce a SC fiber is that the method is scalable to long fiber lengths, and diameter control may be easier than in melt-related methods. To study the feasibility of converting a PC to a SC fiber, we carried out a series of experiments on PC fibers encapsulated in quartz capillary tubes. To convert the extruded fibers to SC fibers, the fibers were heated to slightly above or below the melting point. While this particular approach is not readily scalable to long SC fiber lengths, the information gained in these experiments was useful in developing the prototype SC fiber.

In Figure 3-1 we illustrate the salient features of the growth setup. The 500-μm diameter KRS-5 fiber is placed in a precision bore, fused quartz capillary that is sealed at both ends. The final configuration is designed to pass the tube vertically downward through the heater coils from one to three times at speeds ranging from 1 to 3 mm/h.

When the heater is maintained above the melting point of KRS-5 (410°C), a single-crystal fiber can be fabricated. At temperatures below the melt temperature, the SC regions were observed to propogate for about 1 mm before being interrupted. The surface quality of the melted fibers, however, was generally poor because of wetting between the glass capillary and the fiber, or the presence of entrapped gas.

By removing the quartz capillary and placing the fiber between two sets of synchronously-driven drive wheels (as shown in Figure 3-2), a SC fiber can be prepared by moving the fiber

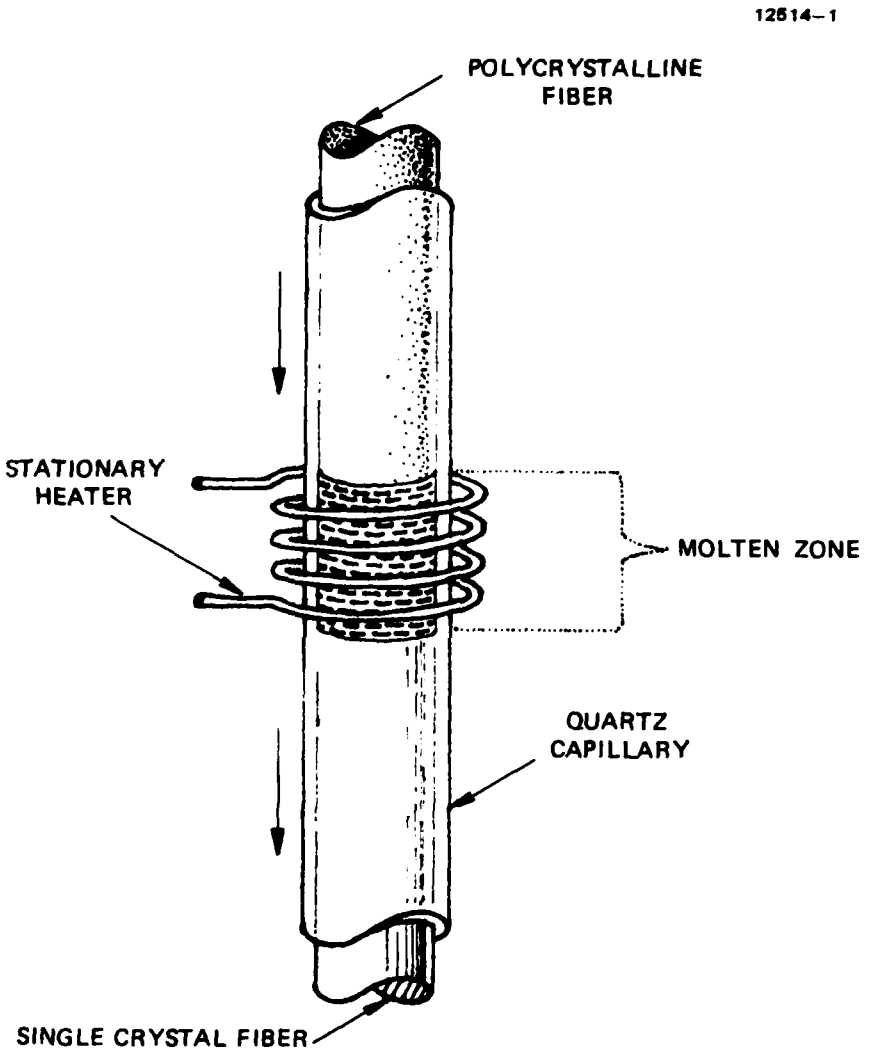

Figure 3-1. Single crystal growth apparatus.

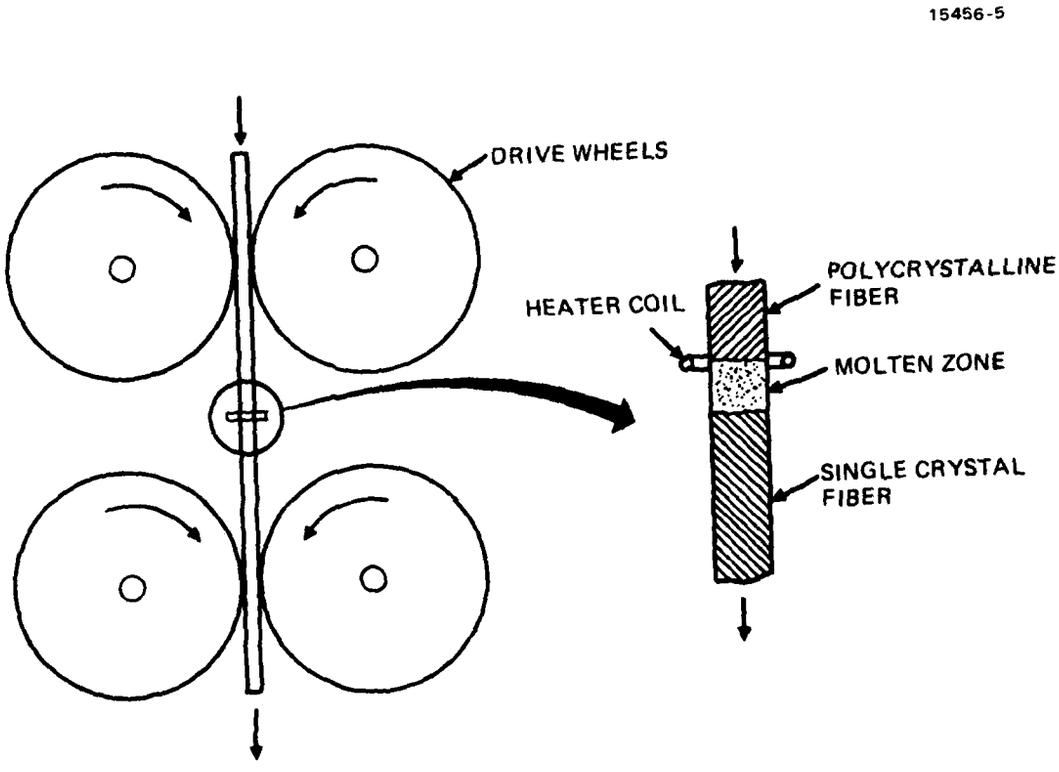

Figure 3-2. Modified single crystal growth apparatus. for unencapsulated fiber.

at approximately 1 cm/min through a heater coil that will melt the fiber for a length of between 0.1 and 4 fiber diameters. The surface tension of the melt zone is high enough to eliminate sagging in the fibers.

Using this technique, (TlBr)I (KRS-5), TlBr, CuCl, AgCl, and AgBr have been converted to single crystal fibers. The thallium salts and CuCl only reacted with the atmosphere during conversion to a single crystal. Although the silver salts were much more stable, future work with this system must be carried out in controlled atmosphere chambers.

Measurements of optical absorption at 10.6 μm for some of the AgBr fiber are shown in Table 3-1. Since the attenuation does not necessarily decrease in the single crystal fiber, it appears that other irregularities in the fiber may play an important role in attenuation.

C. CHALCOGENIDE GLASS FIBERS

Most materials capable of being drawn into fibers for infrared transmission have low softening temperatures and need to be drawn in protective atmospheres. In addition, the proximity of the glass transition temperature (Tg) to the crystallization temperature (Tx) indicates that the furnace must have a sharp hot zone.

Table 3-1. Optical Absorption of AgBr Fiber

15456-6

PC FIBER		SC FIBER	
LENGTH (cm)	LOSS (dB/m)	LENGTH (cm)	LOSS (dB/m)
94	2.6	80	6.6
49	8.5	28	8.3

A furnace capable of drawing heavy-metal fluoride glasses (for an internally funded research program, which was constructed from a NRL design), was incorporated in the present program to draw mixed halide glasses into fiber. A substitution of chalcogenide glass was made for the mixed halide glass toward the end of the program. The chalcogenide glass is commercially available as AMTIR 1 from AMTIR, Inc.

From the viscosity-temperature curve for this gallium arsenic selenide glass, shown in Figure 3-3, it can be seen that the drawing behavior should be the same as for the mixed halide materials. Consequently, this material was drawn into a fiber. Since the drawing characteristics for this glass were relatively stable, long lengths of fiber (~100 m) were made.

Because the material is so brittle, the fiber subsequently started breaking on the drum. Attempts to measure the optical transmission of the fiber were also unsuccessful because the fiber would not bend, without failure, in a 1-m radius of curvature.

In a separate measurement the bulk starting material would not transmit a 10.6-μm beam through a one-inch-thick section.

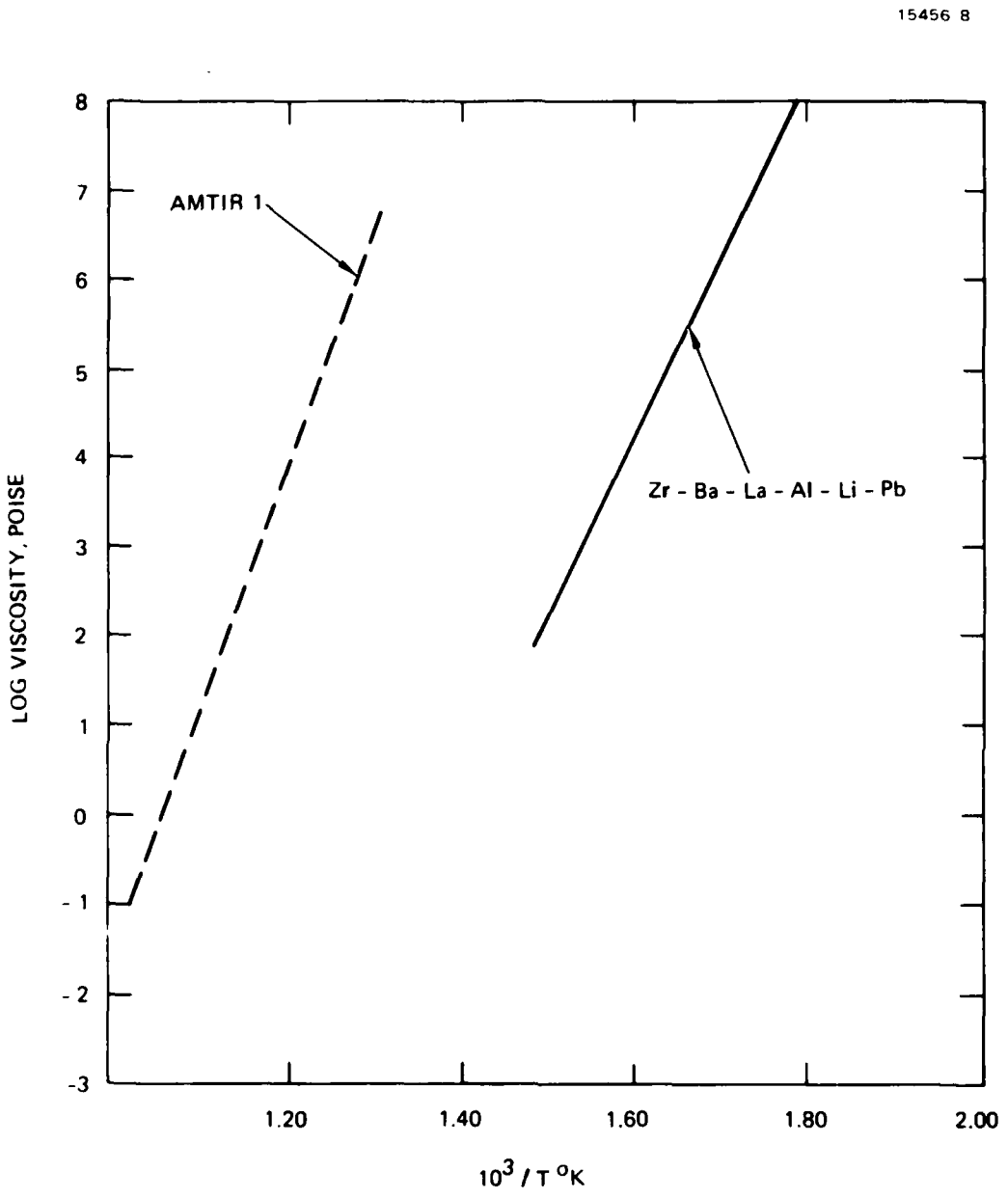

Figure 3-3. Viscosity temperature relationships for both chalcogenide glass and heavy metal fluoride glass.

SECTION 4

FUTURE PLANS AND RECOMMENDATIONS

A. NEW GLASS COMPOSITIONS

Since the completion of this contract in October 1984, progress in the fabrication of new glasses for infrared transmission and fibers from those glasses have been made in a number of laboratories. At HRL, working with internal funding, we have continued to investigate the mixed halide glasses started during this program. From transmission spectra (see Figure 4-1) on glasses with compositions similar to those reported here, we have been able to verify mixed halide glasses with about 90% transmission beyond 11 μm. Additional work is needed to gather information on the glass structure, the crystallization and softening temperatures, and the fiber stability in ambient conditions.

In future work we intend to capitalize on these recent results and investigate the viability of mixed halide glasses for infrared fiber production. In addition, recent investigations of chalcogenide glasses for infrared fiber fabrication have shown that some new compositions appear to be suitable for fiber use. Whenever possible, these new compositions will be fabricated and drawn into fiber to compare with the mixed halide fiber work.

This combination of mixed halide and chalcogenide glass fibers for near to far infrared applications will complement our ongoing work on heavy-metal fluoride glasses for mid to near infrared fiber fabrication.

B. POLYCRYSTALLINE FIBER FABRICATION

The only material that can be somewhat routinely fabricated into a fiber with good mechanical properties and moderately low attenuation at 10.6 μm is KRS-5. Recent investigations at HRL of the mechanisms that could be

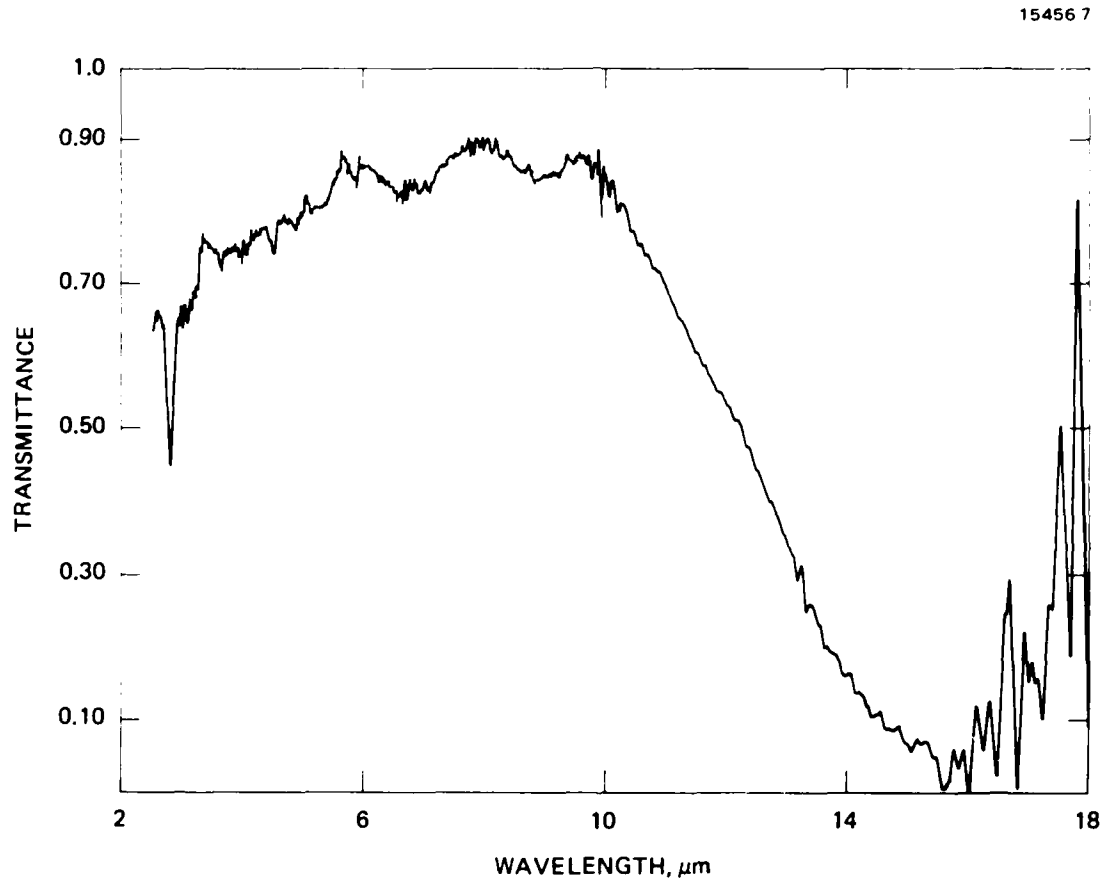

Figure 4-1. Transmission curve for recent mixed halide glass.

accountable for the optical aging reported in this fiber indicate the existence of a stress-assisted surface diffusion. We have arrived at this conclusion after analyzing the results of x-ray and neutron diffraction, Auger, EDAX, and SIMS analyses on both new and old fibers. To complement this work, some aging experiments performed in a variety of atmospheres have demonstrated that it is possible to either accelerate or decelerate the aging process.

Although encouraging, these results do not address the existence of the anamolously high attenuation observed in these fibers which has been the subject of research previously funded by ONR on single-crystal fabrication, cladding techniques and process variables. Since no easy solutions to these problems are available future work should be directed toward fundamental mechanisms. If the time-dependent aging problem can be corrected, these fibers can be used in short distance imaging, power, and data transmission applications that have immediate use in the military. From the study of the mechanisms of the aging problem, we may be able to understand the reasons for the anamolously high attenuation.

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